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(54) **Title:** PERMEABLE CEMENTS

(57) **Abstract:** A permeable cement composition comprises an aqueous slurry of a hydraulic cement including a water-immiscible dispersed fluid phase, such as oil or gas, and a hollow particulate material, the hollow particulate material being one which breaks down in the presence of the cement so as to leave voids which together with the dispersed phase create a permeable structure in the cement.

requirement for post-placement treatments or difficulty in providing or maintaining foams at high downhole pressures or at high foam qualities.

It is an object of the present invention to provide permeable cement compositions that obviate or mitigate some or all of these problems.

One aspect of the invention comprises a permeable cement composition, comprising an aqueous slurry of a hydraulic cement including a water-immiscible dispersed fluid phase and a hollow particulate material, the hollow particulate material being one which breaks down in the presence of the cement so as to leave voids which together with the dispersed phase create a permeable structure in the cement.

The use of a hollow particulate material, such as micro-spheres or cenospheres, allows development of a permeable structure while avoiding the use of very high quantities of the dispersed phase, such as high foam qualities, which can make the slurry difficult to form or place. Such materials, typically formed from aluminosilicate or other glass like materials, break down due to the chemical and thermal environment in the setting cement. In breaking down these materials "release" their porosity and assist in interconnecting the dispersed fluid phase. The exact nature and amount of hollow material used depends upon requirements. A typical material can comprise hollow spheres having average sizes in the range 350 - 50 microns and can be present in amounts of between 10% and 60% by volume of the dry materials used to form the slurry. A suitable source of such hollow materials is the SL range of E-Spheres products from Envirospheres Pty Ltd of Australia. These are available in various size grades, for example 56 micron, 100 – 180 micron, 290 micron and 320 micron.

The water-immiscible dispersed fluid phase can comprise gas such as air or nitrogen, or liquids such as oil. In one embodiment of the invention, the dispersed phase is a gas and the cement slurry is formed as a foam. In another embodiment, the dispersed phase is an oil present as an emulsion in the aqueous slurry.

The hydraulic cement is preferably Portland cement which may or may not include pozzolanic material such as blast furnace slag or fly ash or natural materials such as pozzolana or calcined clays. It is also possible to use high-alumina cements also

fraction can comprise 38% - 50% by volume of the water and solids combined and the oil 40% - 60% by volume of the total.

In the case of an oil emulsion, the use of degradable surfactants can be used to mitigate some of the detrimental effects on the cement setting mechanism. Suitable degradable surfactants are, for example, ethoxylated castor oil surfactants of various ethoxy chain lengths such as those sold by Akzo Nobel under the Berol trade name, e.g. Berol 108, B27, 829 and 192 (in order of decreasing chain length).

Also falling within the scope of the invention are the following remedial applications of the cement compositions described above:

Stopping sand production from a well. When the reservoir is constituted by unconsolidated or poorly consolidated sand, or by poorly bound sandstone or where the formation matrix can be easily dissolved by water, fluid flow into the well entrains grains of sand. The production of sand can lead to a stoppage in well production. To avoid such a situation, a gravel pack or filter screens are normally installed inside the well to stop the sand. Over time, these can become soiled or blocked with fine particles and replacing them is difficult and expensive. Placing a permeable cement according to the invention behind the casing and producing the formation fluids through this layer can prevent sand production into the well and prevent it from becoming necessary to perform the standard operations.

The permeable cement compositions of the invention have the advantage over conventional solutions in that a permeable pack can be made without requiring fluid leakoff to concentrate a solid slurry.

When gravel-packing (or frac-packing) long intervals and/or heterogeneous permeability formations excessive leakoff may occur in certain areas leading to premature screen out and incomplete packing of the annulus. This has previously been overcome by mechanical means (shunt tubes). Permeable cement according to the invention will provide a chemical means to do the same job by being able to form a permeable-pack without requiring leakoff and hence avoiding the potential for screen-

When the strength of the formation is sufficient to allow it, or when the well is highly deviated the cost and/or difficulty related to effectively placing a casing are avoided by carrying out what is known as an uncased or barefoot completion. Sand packing or gravel packing can then be installed if the reservoir might produce sand. A pre-perforated blank liner can also be employed. Placing a layer of permeable cement at the surface of the well walls can avoid the need for such operations. Furthermore, when the formation of the reservoir is not sufficiently strong for that type of simplified completion and it would otherwise have been necessary to put a casing into position with cementing between the casing and the well wall, putting the permeable cement of the invention into position can reinforce the sides of the well and can avoid the need for a casing and subsequent perforation thereof.

When completion with a casing is unavoidable because the rock of the reservoir is very poorly consolidated, placing the permeable cement of the invention between the casing and the sides of the well, instead of a conventional cement, can avoid the need for installing gravel packing or sand packing which is very expensive.

The invention will now be described by way of the following non-limiting examples:

EXAMPLE 1

Slurry A (reference): This slurry corresponds to the prior art. It comprises a class G cement and water such that the density of the slurry is 1900 kg/m^3 (15.8 pounds per gallon, ppg). The slurry is foamed after adding surfactants (aqueous mixture of polyglycols, oxyalkylates and methanol; and a mixture of ethanol, 2 butoxyethanol and ammonium alcohol ethoxysulfate – chain length 6 - 10) in an amount of 0.084 gallons per sack (0.007 l/kg) of powder, to obtain a foam quality of 40% (i.e. the volume of the foam represented 40% of the final volume of the foamed slurry).

The compressive strength and water permeability are measured using samples which are left at ambient temperature and at atmospheric pressure for 48 hours (h) then in an oven at 85°C for 5 days. The compressive strength is expressed in MPa, with pounds per square inch (psi) in brackets.

EXAMPLE 2

The properties of five slurries prepared in accordance with the invention but foamed with different foam qualities are presented and compared:

Basic slurry: A mixture of powders is prepared comprising 30% by volume of haematite particles with a mean size of about 300 microns; 30% by volume of hollow spheres with a mean size of 180 microns; 30% by volume of class G Portland cement and 10% by volume of a Portland/slag micro-cement with a mean size of about 3 microns. Water and a polynaphthalene sulfonate-based super-plasticizer in an amount of 0.07 gallons per sack of powder (0.006 l/kg) are mixed with this powder such that the volume percentage of liquid in the slurry is 40%. Surfactants are added to the basic slurry and the slurries foamed to obtain a foam qualities of 30% to 50% (a foam quality of 30% means that the foam volume represents 30% of the final volume of the slurry).

Slurry	C1	C2	C3	C4	C5
Porosity before foaming	40%	40%	40%	40%	40%
Foam quality	30%	35%	40%	45%	50%
Compressive strength, MPa (psi)	8.27 (1200)	6.90 (1000)	5.59 (810)	4.48 (650)	2.83 (410)
Water permeability (Darcy)	0.0045	0.160	1.2	6.1	>12

The compressive strength and water permeability are measured using samples which are left at ambient temperature and at atmospheric pressure for 48 h then in an oven at 85°C for 5 days.

EXAMPLE 3

The properties of two slurries prepared in accordance with the invention, both containing self-destructive particles but with coarse particles of differing size and nature, are presented and compared:

Slurry D: A mixture of powders is prepared comprising 30% by volume of haematite particles with a mean size of about 300 microns; 30% by volume of hollow cenospheres) with a mean size of 180 microns; 30% by volume of class G Portland cement and 10% by volume of a Portland/slag micro-cement with a mean size of

of powder blend, 0.006 l/kg) are added so that the volume of liquid in the slurry is 45% and the slurry is foamed as above to obtain a foam quality of 40%.

The slurry is heated in a sealed container for two days at 85°C. The resultant cement has a permeability of 1.2 darcy and a compressive strength of 910 psi.

Example 5

A formulation demonstrating that high permeability can be obtained with two particle sizes only and with 40% fine particles.

A powder blend is mixed containing 40% by volume Portland micro-cement/slag, average size 3 microns, 30% hollow spheres of average size 180 microns and 30% hematite of average size 300 microns. Water and polynaphthalene sulphonate dispersant (0.07 gallons per sack of powder blend, 0.006 l/kg) are added so that the volume of liquid in the slurry is 45% and the slurry is foamed as above to obtain a foam quality of 55%.

The slurry is left in a sealed container for two days at ambient temperature and then 5 days in an oven at 85°C. The resultant cement has a permeability of 13 darcy and a compressive strength of 300 psi.

Example 6

A formulation including large particle size cement as some of the large particles giving increased compressive strength whilst retaining significant permeability.

The formulation is identical to C3 above in Example 3 (40% foam, 30% hematite, 30% hollow spheres, 30% cement and 10% micro cement) except that hematite is replaced by large particle cement. Formulation C3 has a permeability of 1.2 darcy and compressive strength of 810 psi. This formulation with hematite replaced by large particle size cement has permeability of 0.62 Darcy but compressive strength increases to 1240 psi.

Example 7

Permeable cement can be made without large particles.

Example 9

A powder base is prepared with 30% cement, 10% micro cement, 50% hollow spheres and 10% large particle size cement. Water is added so as to be 40% by volume of the slurry and a dispersant used as in the foam examples above. Oil is added at 40%, 50% or 60% of volume of total and the surfactant is used at 0.9% by volume of oil added. The slurries are placed in an oven for 2 days at 85°C.

40% oil slurry: permeability to water of 4md, compressive strength =481 psi
50% oil slurry: permeability to water of 78md and a permeability to oil of 249 md, compressive strength to water of 349 psi
60% oil slurry: permeability to water of 61md, compressive strength =138 psi

Increasing the amount of oil allows greater connectivity with other oil droplets and with hollow spheres so as to create a potentially permeable structure. High levels of oil and surfactant can inhibit setting of the cement and hence inhibit the destruction of the hollow spheres which in turn impacts the permeability of the final cement.

Example 10

By using a degradable surfactant the impact on development of a permeable structure as described above can be mitigated.

A powder base is made up with 30% cement, 10% micro cement, 50% hollow spheres and 10% large particle size cement and water is added so as to be 40% by volume of the slurry and dispersant used as in the foam examples above. Three ethoxylated castor oil surfactants are used with decreasing ethoxy- chain lengths – surfactant A > surfactant B > surfactant C. The surfactants are used at 0.06 gallons per sack of powders (0.005 l/kg). Oil is added so as to be 40% of the volume of the total emulsion system. The oil used is a linear alphaolefin. The fluids are placed in an oven for 2 days at 85°C.

Surfactant A system: permeability to water of 0.1 md, compressive strength 618 psi
Surfactant B system: permeability to water of 4.5 md, compressive strength 449 psi
Surfactant C system: permeability to water of 75 md, compressive strength 1208 psi

CLAIMS

1 A permeable cement composition, comprising an aqueous slurry of a hydraulic cement including a water-immiscible dispersed fluid phase and a hollow particulate material, the hollow particulate material being one which breaks down in the presence of the cement so as to leave voids which together with the dispersed phase create a permeable structure in the cement.

2 A cement composition as claimed in claim 1, wherein the hollow particulate material comprises micro-spheres or cenospheres.

3 A cement composition as claimed in claim 1 or 2, wherein the hollow particulate material has particles sizes in the range 350 – 50 microns.

4 A cement composition as claimed in any of claims 1 – 3, wherein the hollow particulate material is present in an amount of 10% - 60% by volume of dry materials used to make the slurry.

5 A cement composition as claimed in any preceding claim, wherein the dispersed fluid phase comprises air, nitrogen or oil.

6 A cement composition as claimed in any preceding claim, wherein the cement comprises Portland cement, pozzolanic material, blast furnace slag, fly ash, pozzolana, calcined clays, high-alumina cements, plaster, Sorel cement, or activated pozzolanic cements.

7 A cement composition as claimed in any preceding claim, wherein the slurry comprises solid materials including a combination of at least two of a fine particulate material having particle sizes in the range 0.1 – 10 micron, a medium particulate material having particle sizes in the range 20 – 60 micron and a coarse particles having particle sizes in the range 100 – 800 micron.

8 A cement composition as claimed in claim 7, wherein the fine particulate material comprises micro-cement.

18 A cement composition as claimed in any of claims 1 – 16, wherein when the dispersed phase comprises oil, the slurry comprises 38% - 50% by volume of an aqueous phase and 40% - 60% by volume of the total of oil.

19 A cement composition as claimed in any preceding claim, wherein the slurry further comprises a degradable surfactant.

20 A cement composition as claimed in claim 19, wherein the degradable surfactant comprises an ethoxylated castor oil.

21 A cement composition as claimed in any of claims 1 – 18, wherein the slurry further comprises a surfactant with a cloud point.

22 A method of remedial treatment of voids behind casing in a borehole, comprising pumping a cement slurry into the void and allowing it to set, the cement slurry comprising an aqueous slurry of a hydraulic cement including a water-immiscible dispersed fluid phase and a hollow particulate material, the hollow particulate material being one which breaks down in the presence of the cement so as to leave voids which together with the dispersed phase create a permeable structure in the cement.

23 A method of completing a well, comprising pumping a cement slurry into an annulus around a casing, screen or slotted liner placed in a well and allowing it to set, the cement slurry comprising an aqueous slurry of a hydraulic cement including a water-immiscible dispersed fluid phase and a hollow particulate material, the hollow particulate material being one which breaks down in the presence of the cement so as to leave voids which together with the dispersed phase create a permeable structure in the cement.

24 A method of preventing sand production from an underground formation into a well, comprising pumping a cement slurry into a region adjacent the formation and allowing it to set, the cement slurry comprising an aqueous slurry of a hydraulic cement including a water-immiscible dispersed fluid phase and a hollow particulate material, the hollow particulate material being

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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